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(54) RESIN SOLUTIONS

(71) We, MONSANTO COMPANY, a corporation organised under the laws of the State of Delaware, United States of America, of 800 North Lindbergh Boulevard, St. Louis, Missouri 63166, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a pressure-sensitive resin solution and specifically to an organic solvent solution containing a chelate ester of orthotitanic acid and a resin with a functional group capable of reaction with the ester. In another aspect, the invention relates to a process for the manufacture of an article containing a film of pressure-sensitive resin.

Pressure-sensitive resins are used conventionally in the form of films to provide adhesive bonds between normally non-adhering substrates and substrates. The films may be prepared by casting them from organic solvent solutions and evaporating the solvent.

Constraints are placed on the molecular weight of the pressure-sensitive resin by the viscosity of the solution necessary for ease of coating on commercial coating machines and by the solution concentration required for economical operation. In general, low solution viscosity and high solution concentration are desired in the pressure-sensitive resin solution, and, hence, a resin of relatively low molecular weight is preferred for film casting.

Once a bond has been made by a pressure-sensitive film placed between a substrate and a superstrate, the pressure-sensitive film may be subjected to stress generated by the weight of the superstrate or by dimensional change in the substrate or superstrate caused by thermal expansion, stress relaxation, plasticizer migration or the like. In general, a high molecular weight and a high cohesive strength is desired in the pressure-sensitive resin so that it may resist the stresses induced in the adhesive film. The opposing requirements of low molecular weight resin for ease of coating and high molecular weight resin for load holding ability are conventionally reconciled by the use of crosslinkable resin systems which can be applied at low molecular weight and cured to a high molecular weight.

Metal alkoxides are taught by Blance in U.S. Patent 3,532,708 as crosslinking agents for solution pressure-sensitive adhesives. They offer the potential of cure at room temperature merely by evaporation of the solvent. Of particular interest have been tetra-alkyl titanates which are formulated with hydroxy pressure-sensitive resins in alcohol solutions to yield stable solutions from which crosslinked pressure-sensitive resins are obtained by evaporation of the alcoholic solvent. However, such titanates particularly the lower alkyl titanates impart high solution viscosity and undesirable flow to the resin solutions.

The undesirable flow is manifested by the tendency of the resin solution to form a highly extended "string" or column of fluid when a spatula or like object is pulled rapidly out of the solution. Solutions exhibiting such "stringiness" are difficult to apply on modern high-speed coating machinery. Uneven splitting and transfer of the adhesive solution on the rolls causes uneven coating. On reverse roll coaters, the formation of strings at the roll nips produces a ribbed effect in the coating and on gravure rolls, webs of solution produce coating defects.

There is, therefore, a need in the art for pressure-sensitive resin solutions with suitable viscosity and flow for application by coating rolls and which yield

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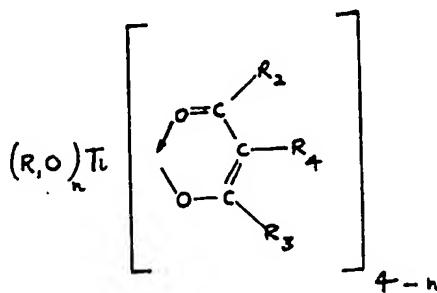
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pressure-sensitive resins curable at room temperature or at slightly elevated temperatures to yield adequate cohesive strength.

The present invention provides an organic solvent solution comprising,
(i) a chelate ester having the formula

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wherein n is 2 or 3, R₁ is a C₂ to C₁₀ alkyl, alkenyl, substituted alkyl or substituted alkenyl group, R₂ is a C₁ to C₆ alkyl, alkoxy, alkenyl or alkenoxy group, R₃ is a C₁ to C₆ alkyl or alkenyl group or a C₆ to C₁₀ aryl group and R₄ is hydrogen or a C₁ to C₆ alkyl or alkenyl group, and R₂ and R₃ may be combined as an ethylene or a trimethylene group; and

10 (ii) an interpolymer comprising:

(A) between 0.5 and 20 weight per cent of at least one monomer containing a hydroxyl, carboxyl or enolizable keto group,

(B) at least one monomer which is an ester of acrylic acid or methacrylic acid containing from 6 to 20 carbon atoms, and optionally

15 (C) a monomer which is an α -olefin containing from 2 to 10 carbon atoms, a C₃ to C₁₀ vinyl alkoate, an ethyl or methyl ester of acrylic or methacrylic acid, acrylonitrile, methacrylonitrile, styrene, or vinyl chloride, wherein the interpolymer has a weight average molecular weight in the range of 10,000 to 500,000 and a glass transition

20 temperature in the range of -15 to -75°C.;

wherein there are between 0.01 and 4 parts by weight of the chelate ester per 100 parts of interpolymer and wherein the stringiness index of the solution is less than 0.76 cm.

25 The invention further provides a process for preparing pressure-sensitive resin solutions with improved viscosity and flow and a process for coating them as films on substrates to provide articles of manufacture comprising films of pressure-sensitive interpolymer containing the abovedescribed chelate esters of orthotitanic acid.

30 The practice of the present invention involves the preparation of the interpolymer which is then formulated with the chelate ester of orthotitanic acid in a suitable organic solvent. The solution is cast on a substrate, the organic solvent is dispelled and the resulting film is cured to a creep-resistant permanently tacky composition.

35 The interpolymer comprises monomers selected from the groups A, B, and C described above. Group A monomers contain hydroxyl, carboxyl or enolizable keto groups. Monomers containing hydroxyl groups are exemplified by hydroxyalkyl acrylates, methacrylates, fumarates or maleates wherein the hydroxy alkyl group contains from 2 to 4 carbon atoms. Preferred hydroxy monomers include 2-hydroxyethyl acrylate or methacrylate, 2-hydroxypropyl acrylate or methacrylate, 3-hydroxypropyl acrylate or methacrylate, or bis(2-hydroxyethyl)fumarate or maleate. Monomers containing carboxyl groups are exemplified by acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, and the like, maleic acid, fumaric acid, citraconic acid, itaconic acid, and the like, and the alkyl monoesters of maleic acid, fumaric acid, citraconic acid and itaconic acid in which the alkyl group contains from 1 to 8 carbon atoms such as methyl, ethyl, propyl, butyl and octyl maleates and the like. Preferred acid monomers include acrylic acid and methacrylic acid. Monomers containing enolizable keto groups include N,N-diacetonylacrylamide and N,N-diacetonylmethacrylamide. The amount of group A monomer in the interpolymer is in the range of 0.5 to 20 weight per cent of the interpolymer, and is preferably in the range of 1 to 10 per cent for adequate crosslinking potential without excessive solution viscosity.

40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240 245 250 255 260 265 270 275 280 285 290 295 300 305 310 315 320 325 330 335 340 345 350 355 360 365 370 375 380 385 390 395 400 405 410 415 420 425 430 435 440 445 450 455 460 465 470 475 480 485 490 495 500 505 510 515 520 525 530 535 540 545 550 555 560 565 570 575 580 585 590 595 600 605 610 615 620 625 630 635 640 645 650 655 660 665 670 675 680 685 690 695 700 705 710 715 720 725 730 735 740 745 750 755 760 765 770 775 780 785 790 795 800 805 810 815 820 825 830 835 840 845 850 855 860 865 870 875 880 885 890 895 900 905 910 915 920 925 930 935 940 945 950 955 960 965 970 975 980 985 990 995 1000 1005 1010 1015 1020 1025 1030 1035 1040 1045 1050 1055 1060 1065 1070 1075 1080 1085 1090 1095 1100 1105 1110 1115 1120 1125 1130 1135 1140 1145 1150 1155 1160 1165 1170 1175 1180 1185 1190 1195 1200 1205 1210 1215 1220 1225 1230 1235 1240 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2245 2250 2255 2260 2265 2270 2275 2280 2285 2290 2295 2300 2305 2310 2315 2320 2325 2330 2335 2340 2345 2350 2355 2360 2365 2370 2375 2380 2385 2390 2395 2400 2405 2410 2415 2420 2425 2430 2435 2440 2445 2450 2455 2460 2465 2470 2475 2480 2485 2490 2495 2500 2505 2510 2515 2520 2525 2530 2535 2540 2545 2550 2555 2560 2565 2570 2575 2580 2585 2590 2595 2600 2605 2610 2615 2620 2625 2630 2635 2640 2645 2650 2655 2660 2665 2670 2675 2680 2685 2690 2695 2700 2705 2710 2715 2720 2725 2730 2735 2740 2745 2750 2755 2760 2765 2770 2775 2780 2785 2790 2795 2800 2805 2810 2815 2820 2825 2830 2835 2840 2845 2850 2855 2860 2865 2870 2875 2880 2885 2890 2895 2900 2905 2910 2915 2920 2925 2930 2935 2940 2945 2950 2955 2960 2965 2970 2975 2980 2985 2990 2995 3000 3005 3010 3015 3020 3025 3030 3035 3040 3045 3050 3055 3060 3065 3070 3075 3080 3085 3090 3095 3100 3105 3110 3115 3120 3125 3130 3135 3140 3145 3150 3155 3160 3165 3170 3175 3180 3185 3190 3195 3200 3205 3210 3215 3220 3225 3230 3235 3240 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7245 7250 7255 7260 7265 7270 7275 7280 7285 7290 7295 7300 7305 7310 7315 7320 7325 7330 7335 7340 7345 7350 7355 7360 7365 7370 7375 7380 7385 7390 7395 7400 7405 7410 7415 7420 7425 7430 7435 7440 7445 7450 7455 7460 7465 7470 7475 7480 7485 7490 7495 7500 7505 7510 7515 7520 7525 7530 7535 7540 7545 7550 7555 7560 7565 7570 7575 7580 7585 7590 7595 7600 7605 7610 7615 7620 7625 7630 7635 7640 7645 7650 7655 7660 7665 7670 7675 7680 7685 7690 7695 7700 7705 7710 7715 7720 7725 7730 7735 7740 7745 7750 7755 7760 7765 7770 7775 7780 7785 7790 7795 7800 7805 7810 7815 7820 7825 7830 7835 7840 7845 7850 7855 7860 7865 7870 7875 7880 7885 7890 7895 7900 7905 7910 7915 7920 7925 7930 7935 7940 7945 7950 7955 7960 7965 7970 7975 7980 7985 7990 7995 8000 8005 8010 8015 8020 8025 8030 8035 8040 8045 8050 8055 8060 8065 8070 8075 8080 8085 8090 8095 8100 8105 8110 8115 8120 8125 8130 8135 8140 8145 8150 8155 8160 8165 8170 8175 8180 8185 8190 8195 8200 8205 8210 8215 8220 8225 8230 8235 8240 8245 8250 8255 8260 8265 8270 8275 8280 8285 8290 8295 8300 8305 8310 8315 8320 8325 8330 8335 8340 8345 8350 8355 8360 8365 8370 8375 8380 8385 8390 8395 8400 8405 8410 8415 8420 8425 8430 8435 8440 8445 8450 8455 8460 8465 8470 8475 8480 8485 8490 8495 8500 8505 8510 8515 8520 8525 8530 8535 8540 8545 8550 8555 8560 8565 8570 8575 8580 8585 8590 8595 8600 8605 8610 8615 8620 8625 8630 8635 8640 8645 8650 8655 8660 8665 8670 8675 8680 8685 8690 8695 8700 8705 8710 8715 8720 8725 8730 8735 8740 8745 8750 8755 8760 8765 8770 8775 8780 8785 8790 8795 8800 8805 8810 8815 8820 8825 8830 8835 8840 8845 8850 8855 8860 8865 8870 8875 8880 8885 8890 8895 8900 8905 8910 8915 8920 8925 8930 8935 8940 8945 8950 8955 8960 8965 8970 8975 8980 8985 8990 8995 9000 9005 9010 9015 9020 9025 9030 9035 9040 9045 9050 9055 9060 9065 9070 9075 9080 9085 9090 9095 9100 9105 9110 9115 9120 9125 9130 9135 9140 9145 9150 9155 9160 9165 9170 9175 9180 9185 9190 9195 9200 9205 9210 9215 9220 9225 9230 9235 9240 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containing from 6 to 20 carbon atoms. Preferred esters contain branched chain alkyl groups such as isobutyl acrylate, 2-ethylhexyl acrylate and 2-ethylhexyl methacrylate. The pressure-sensitive resin need only contain monomers from groups A and B. However, optionally, monomers from Group C may also be present. Group C includes α -olefins containing from 2 to 10 carbon atoms, C₃ to C₁₀ vinyl alkanoates such as vinyl acetate and vinyl octoate, ethyl and methyl esters of acrylic and methacrylic acids, acrylonitrile, methacrylonitrile, styrene and vinyl chloride.

The ratio of monomers in the interpolymer is selected so that the glass transition temperature is in the range of -15 to -75°C. A suitable ratio is conventionally calculated from the equation:

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} + \dots + \frac{W_n}{T_{gn}}$$

where T_g is the glass transition temperature of the interpolymer expressed as degrees Kelvin, T_{g1}, T_{g2}, etc. are the glass transition temperatures of the homopolymers of the respective comonomers and W₁, W₂, etc. are the weight fractions of comonomers required for a specific glass transition temperature of the interpolymer. Glass transition temperatures are determined experimentally by conventional methods such as by means of the duPont Differential Thermal Analyzer.

The weight average molecular weight of the interpolymer is in the range of 10,000 to 500,000, corresponding to a relative viscosity in the range of 1.3 to 8.0 measured on a solution of 2 grams of interpolymer per deciliter of benzene. The preferred molecular weight range is from 20,000 to 300,000, providing adequate cohesive strength to the interpolymer without excessive solution viscosity.

The interpolymers are conveniently prepared by organic solvent polymerization techniques involving in some cases delayed addition of monomer when there is a great disparity between reactivity ratios as for example between the reactivity ratios of vinyl acetate and acrylate monomers. The time interval for the delayed addition may range from about 60 to about 600 minutes and longer. The techniques in general, involve the polymerization of the respective monomer mixtures in suitable organic solvents, the polymerization being initiated by heat activated free radical initiators.

The choice of solvents for the interpolymer used in the practice of this invention is governed by the solubility requirements of the monomers and the resulting interpolymers in that both the monomers and the resulting interpolymers should be soluble in the selected solvent or mixtures of solvents. A further preferred requirement is that the interpolymer solution should contain less than 3 per cent water by weight, based on the total weight of the solvent, in order to avoid adverse interference with the metal alkoxide component. More preferably, the interpolymer solution should contain less than 2 per cent water by weight.

Examples of suitable solvents for the interpolymers include aromatic solvents such as benzene, toluene and xylene. Suitable aliphatic solvents include esters such as ethyl acetate, propyl acetate, isopropyl acetate, butyl acetate, etc.; ketones such as methyl ethyl ketone, acetone, etc.; aliphatic hydrocarbons such as hexane and pentane. Especially useful are mixtures of the foregoing.

The polymer systems of this invention may also be prepared in mass or non-aqueous dispersion type polymerization processes as are well known to those skilled in the art. However, solution polymerization processes are preferred.

Polymerization initiators suitable for the preparation of the special interpolymers of this invention include organic peroxides, such as tert-butyl hydroperoxide, di-tert-butylperoxide, cumene hydroperoxide, di-cumyl peroxide and benzoyl peroxide. Equally suitable are organic peroxygen compounds such as tert-butyl peracetate, tert-butyl perbenzoate, di-tert-butyl perphthalate; other initiators would include α,α' -azo-di-isobutyronitrile, ultraviolet light, gamma radiation, etc.

The following preparation Examples 1 to 11 illustrate the preparation formulation and testing of the special interpolymers which are to be used in the practice of this invention and Examples A, B and C illustrate the invention. All parts and percentages are by weight unless otherwise specified and the expressions polymer and interpolymer are used interchangeably.

Preparation Example 1.

This preparation Example illustrates the preparation of an interpolymer comprising 50.5 parts 2-ethylhexyl acrylate, 45 parts methyl acrylate and 4.5 parts 2-hydroxyethyl acrylate.

5 The polymer is prepared under reflux conditions in a kettle equipped with a stirrer, condenser, holding tanks and pumps. 5

AMOUNT OF INGREDIENTS, Parts by Weight

	Initial Charge	Subsequent charges		
		1	2	3
2-ethylhexyl acrylate	14.1		6.97	
Methyl acrylate	12.6		6.20	
2-hydroxyethyl acrylate	1.26		0.62	
Ethyl acetate	19.69	12.3		9.0
Hexane	5.14		2.74	9.26
α, α' -azo-diisobutyronitrile	0.076	0.038		
Dodecyl mercaptan	0.0027	0.0013		

10 Charges 1 and 2 are made at uniform rates over the 14 hour period after the initial charge reaches reflux. After 6½ hours of reflux, the batch is cooled and charge 3 is added. The solids content is 41.0 per cent. The Brookfield viscosity is 3,000 cps. The relative viscosity, determined with a solution of 2 grams of resin in 100 ml. benzene is 4.1. 10

15 Preparation Examples 2 to 11. The general procedure of preparation Example 1 is followed except that different monomers and monomer ratios are used in order to illustrate a variety of interpolymers used in the practice of this invention. 15

TABLE 1.
COMPOSITIONS OF INTERPOLYMERS
PREPARED IN PREPARATION EXAMPLES 1 to 11.

Prep. Ex.	Monomeric Components	Weight Ratio
1	EHA/MA/HEA	50.5/45/4.5
2	EHA/VAc/AA	59/39.5/1.5
3	EHA/VAc/AA	52/47/1.0
4	EHA/MA/AA	61/33/6.2
5	EHA/MA/HEA	71/24/5
6	iBA/MA/HEA	71/24/5
7	VAc/EHA/HPA	45/50/5
8	VAc/EHA/HEMA	35/60/5
9	VAc/EHA/HEF	40/55/5
10	AN/EHA/HEMA	25/70/5
11	VCl/EHA/HEMA	30/65/5

LEGEND

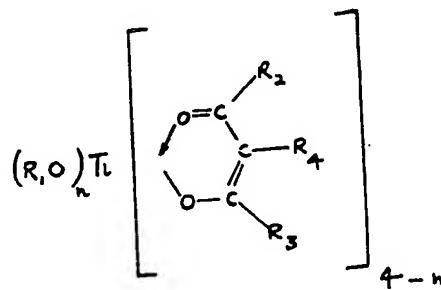
EHA	2-ethylhexyl acrylate
MA	methyl acrylate
HEA	2-hydroxyethyl acrylate
VAc	vinyl acetate
AA	acrylic acid
HPA	3-hydroxypropyl acrylate
HEMA	2-hydroxyethyl methacrylate
HEF	bis-(2-hydroxyethyl)fumarate
AN	acrylonitrile
VCl	vinyl chloride
iBA	isobutyl acrylate

TABLE 2.
SOLUTION PROPERTIES OF INTERPOLYMERS
OF PREPARATION EXAMPLES 1 to 11

SOLVENT, Weight %

Prep. Ex.	Ethyl Acetate	Toluene	Hexane	iPrOH	EtOH	Solids, %	Viscosity, cps.	Relative Viscosity
1	70	—	30	—	—	41	3,000	4.1
2	50	—	50	—	—	50	15,000	2.7
3	10	19	71	—	—	56	30,000	3.2
4	75	—	15	10	—	39	15,000	4.3
5	70	—	20	10	—	41	5,200	4.7
6	60	20	—	—	20	41	12,000	—
7	74	—	18	—	8	42	8,800	5.7
8	74	—	—	—	26	40	8,500	—
9	74	—	—	—	26	43	9,200	—
10	20	80	—	—	—	37	—	—
11	100	—	—	—	—	41	—	—

After the preparation of the interpolymer, the interpolymer solution is formulated with at least one chelate ester of orthotitanic acid of the general formula:



5 wherein n is an integer of 2 or 3, R₁ is a C₂ to C₁₀ alkyl, alkenyl, substituted alkyl or substituted alkenyl group, R₂ is a C₁ to C₆ alkyl, alkoxy, alkenyl or alkenoxy group, R₃ is a C₁ to C₆ alkyl or alkenyl group or a C₆ to C₁₀ aryl group and R₄ is hydrogen or a C₁ to C₆ alkyl or alkenyl group, and R₂ and R₃ may be combined as an ethylene or a trimethylene group.

10 The chelate esters are prepared by conventional methods such as the addition of the appropriate chelating agent to an alkyl or alkenyl titanate wherein the alkyl or alkenyl group contains 2 to 10 carbon atoms. Among the chelating agents which can be used are, for example, acetylacetone, propionylacetone, benzoylacetone, 1,3-cyclopentandione, 1,3-cyclohexandione, alkyl acetoacetates, such as ethyl acetoacetate, and the alkyl and alkenyl substituted derivatives of these diketones and acetoacetates. Thus, where acetylacetone is used as the chelating agent the R₂ and R₃ groups are methyl and the R₄ group is hydrogen. The chelating agents may be reacted with the lower alkyl or alkenyl titanate in a molar ratio ranging from 1:1 to 2:1. The preferred ratio is about 2:1 so that, for example, when acetylacetone is used, a dialkoxy titanium diacetylacetone is obtained. The alkanol generated by the reaction may be distilled. Alternatively, it may be allowed to remain so that the product of reaction is essentially a solution of chelate ester in alkanol. The preferred chelate esters are dialkoxy titanium diacetylacetones, dialkyl titanium di(1,3-cyclopentandionates) and dialkoxy titanium di(1,3-cyclohexandionates).

15 25 The amount of chelate ester used in a given resin solution will depend on the type of reactive group in the interpolymer, the molecular weight of the interpolymer, the concentration of interpolymer in the solution, the composition of the solvent and the degree of crosslinking desired in the pressure-sensitive resin after it has been cast from solution. As little as 0.01 parts by weight of the chelate ester per 100 parts by weight of interpolymer can give a significant effect on the cohesive strength of the polymer as measured by the creep resistance. As much as 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240 245 250 255 260 265 270 275 280 285 290 295 300 305 310 315 320 325 330 335 340 345 350 355 360 365 370 375 380 385 390 395 400 405 410 415 420 425 430 435 440 445 450 455 460 465 470 475 480 485 490 495 500 505 510 515 520 525 530 535 540 545 550 555 560 565 570 575 580 585 590 595 600 605 610 615 620 625 630 635 640 645 650 655 660 665 670 675 680 685 690 695 700 705 710 715 720 725 730 735 740 745 750 755 760 765 770 775 780 785 790 795 800 805 810 815 820 825 830 835 840 845 850 855 860 865 870 875 880 885 890 895 900 905 910 915 920 925 930 935 940 945 950 955 960 965 970 975 980 985 990 995 1000 1005 1010 1015 1020 1025 1030 1035 1040 1045 1050 1055 1060 1065 1070 1075 1080 1085 1090 1095 1100 1105 1110 1115 1120 1125 1130 1135 1140 1145 1150 1155 1160 1165 1170 1175 1180 1185 1190 1195 1200 1205 1210 1215 1220 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In the evaluation of pressure-sensitive resin solutions containing esters of orthotitanic acid, the solutions are formulated to 32 weight per cent solids. The

esters of orthotitanic acid are added in ethanol solution gradually with stirring to the pressure-sensitive resin solution, the amount of ethanol being 25 weight per cent of the total solvent in the final solution.

5 The solutions are subjected to determination of viscosity and "stringiness index". Viscosity is determined at 20°C. by the conventional method using a Brookfield Model LVF Viscometer and the appropriate spindle and speed. Viscosity stability is determined from viscosity measurements over a 7 day period.

10 The stringiness index (S.I.) is determined by immersing a platinum surface tension ring of 3.6 cm diameter, one inch below the surface of the pressure-sensitive resin solution contained in a 7.62 cm diameter jar. The ring is mounted in the jaw of an Instron Test Machine and is withdrawn from the solution by allowing the crosshead upon which the jar rests to descend at a rate of 12.7 cm/min. ("INSTRON" is a registered Trade Mark). The tensile force exerted on the ring is recorded by means of the A cell on the chart set at 10 grams full scale and moving at 12.7 cm/min. The stringiness index is measured from the peak of maximum extensional force to the failure point of the elongating curtain of solution. Five measurements are made in rapid succession. The arithmetic average expressed in centimetres is the stringiness index. In general, a stringiness index of less than 0.76 cm indicates that a resin solution has good flow properties and that the solution will not form strings on conventional high-speed roll coaters at normal speeds of operation. The tendency of a pressure-sensitive resin solution to develop stringiness is determined by measurement of the stringiness index over a 7 day period.

EXAMPLE A.

25 The data for viscosity and stringiness index of the interpolymer solutions of preparation Examples 1—4 formulated with various esters of orthotitanic acid are presented in Tables 3 and 4. The solids content of the solutions is 32 per cent. Ethanol forms 25 per cent of the solvent. In the Tables, TBT signifies tetrabutyl titanate and TAA signifies di-isopropoxy titanium diacetylacetone which is formed by reaction of 2 moles of acetylacetone with 1 mole of tetra-isopropyl titanate.

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TABLE 3.
EFFECT OF TITANATE TYPE ON SOLUTION VISCOSITIES (viscosities in cps.)
RESIN

Concentration, grams per 100 g. resin	Titanate	Prep. Example 1		Prep. Example 2		Prep. Example 3		Prep. Example 4	
		Type	Initial	Aged 1 week	Initial	Aged 1 week	Initial	Aged 1 week	Initial
0	none	800	850	195	180	375	380	—	—
0.2	TBT	1,170	1,140	270	280	535	560	—	—
	TAA	810	840	235	240	415	410	—	—
0.4	TBT	1,920	1,800	470	500	1,110	1,200	Gel	Gel
	TAA	870	900	300	345	450	460	7,700	14,000
0.6	TBT	Gel	Gel	1,130	1,350	2,550*	3,000*	Gel	Gel
	TAA	940	1,000	250	455	480	480	9,000	18,000

* Veryropy, stringy; not coatable.

TABLE 4.
EFFECT OF TITANATE TYPE ON "STRINGINESS INDEX" (in inches)
RESIN

Concentration, grams per 100 g. resin	Titanate	Prep. Example 1		Prep. Example 2		Prep. Example 3		Prep. Example 4	
		Type	Initial	Aged 1 week	Initial	Aged 1 week	Initial	Aged 1 week	Initial
0	None	0.18	0.21	0.23	0.19	0.13	0.14	0.14	0.14
0.2	TBT	0.22	0.25	0.21	0.30	0.14	0.17	—	—
	TAA	0.18	0.21	0.20	0.29	0.18	0.18	0.18	0.18
0.4	TBT	0.35	0.27	0.37	0.41	0.21	0.20	—	—
	TAA	0.20	0.19	0.18	0.26	0.18	0.18	0.18	0.18
0.6	TBT	—	—	0.39	0.53	0.64	0.72	—	—
	TAA	0.20	0.22	0.22	0.27	0.18	0.18	0.18	0.18

The data show the higher viscosities, the tendency to gel and the higher stringiness indices of pressure-sensitive resin solutions containing tetrabutyl titanate in comparison with solutions containing diisopropoxy titanium diacetylacetonate especially at higher concentrations of the titanate ester.

5 Data for stringiness index of interpolymer solutions of preparation Examples 3 and 6 through 11 formulated with various chelate esters of orthotitanic acid are presented in Table 5. The solids content of the solutions is 30 per cent. Ethanol forms 25 per cent of the solvent. The concentration of chelate ester of titanium is 0.4 parts per 100 parts by weight of resin.

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EXAMPLE B.

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The pressure-sensitive resin solutions listed in Table 3 are cast on silicone release paper, and the cast films are dried at room temperature then at 90°C. for 2 minutes to dispel the organic solvent. The (0.002 cm thickness) films are cooled to room temperature and applied to polyvinyl chloride film (Ultron Polyvinyl Chloride UL-58 Film, 0.0076 cm thick, supplied by Monsanto Company). The laminate is cut into 2.54 cm strips. The strips are conditioned at 22°C and 50% relative humidity for 24 hours. The release paper is removed and the strips are applied to steel panels (ASTM 1000-65) with a Pressure-Sensitive Tape Council roller. Peel strength is determined on an Instron Test Machine by peeling the strip at a 180° angle and at a rate of 15.1 cm per minute from the steel panel. "Green" strength is gauged by comparing the peel strength of the bond 20 minutes after formation and 24 hours after formation. Data are presented in Table 6.

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TABLE 5.

STRINGINESS INDEX OF INTERPOLYMER SOLUTIONS CONTAINING CHELATE ESTERS OF ORTHOTITANIC ACID

TITANIUM CHELATE ESTER				
Resin Prep. Ex.	n	R ₁	Chelating Agent	Stringiness Index (cm)
3	2	iso-propyl	acetylacetone	<0.76 cm
6	3	iso-propyl	acetylacetone	<0.76 cm
7	2	octyl	benzoylacetone	<0.76 cm
8	2	butyl	1,3-cyclohexanedione	<0.76 cm
9	2	octyl	1,3-cyclopentanedione	<0.76 cm
10	2	butyl	ethyl acetoacetate	<0.76 cm
11	2	iso-propyl	acetylacetone	<0.76 cm

TABLE 6.
PEEL STRENGTH OF PRESSURE-SENSITIVE RESINS (gm/cm
width)

Titanate	Concentration, grams per 100 g. resin	Type	Prep. Example 1			Prep. Example 2			Prep. Example 3		
			20 min.	24 hr.	20 min.	24 hr.	20 min.	24 hr.	20 min.	24 hr.	24 hr.
0	none		678.7	714.4	893.0	1536.0 ^c *	750.1	839.4			
0.2	TBT	589.4	714.0	714.0	1250.2 ^c *	696.5	785.8				
	TAA	607.2	678.7	660.8	1339.5 ^c *	643.0	821.6				
0.4	TBT	535.8	696.5	553.7	857.3	660.8	750.1				
	TAA	535.8	750.1	535.8	982.3	571.5	750.1				
0.6	TBT	535.8	625.1	446.5	785.8	517.9	714.0				
	TAA			482.2	863.7						

* Subscript "c" denotes cohesive splitting of the film.

The data show that titanate ester causes a decrease in peel strength in direct relation to the concentration of titanate ester. However, the effects of tetrabutyl titanate and diisopropoxy titanium diacetylacetone are essentially equivalent and in no case is the peel strength reduced below a useful value.

5 The cohesive strength of the pressure-sensitive adhesive is gauged from the

creep resistance of a 1.61 cm² 0.002 cm thick bond formed by the film of adhesive between a strip of Mylar Polyester film (a product of E. I. duPont de Nemours and Company) and a polished stainless steel bar ("MYLAR" is a registered Trade Mark). The Mylar strip is loaded with a one-pound weight. The bond is held in a vertical plane at 22°C and 50% relative humidity and the time in hours for failure after application of the load is determined. The data are presented in Table 7.

TABLE 7.
CREEP RESISTANCE OF PRESSURE-SENSITIVE RESINS
(hours to failure)

Concentration, g. per 100 g. resin	Type	RESIN			
		Pr. Ex. 1	Pr. Ex. 2	Pr. Ex. 3	Pr. Ex. 4
0	none	0.2	0.3	0.7	0.5
0.2	TBT	3	3	4.6	—
	TAA	3	2	4	10
0.4	TBT	10	55	40	—
	TAA	25	15	55	25
0.6	TBT	—	52	—	—
	TAA	55	145	155	—

Note that at low concentrations of titanate ester, the initial creep resistance is roughly the same for resins containing tetrabutyl titanate and those containing diisopropoxy titanium diacetylacetone; but at higher concentrations, the creep resistance improves to a higher level for TAA formulations than for the TBT systems. An exception is the preparation Example 2 system for which TBT may be a more efficient crosslinker.

This invention also contemplates the use of fillers, extenders, stabilizers, antioxidants, plasticizers, tackifiers, flow control agents, adhesion promoters, dyes, etc. in the pressure-sensitive resin solutions and the pressure-sensitive resins of this invention.

The compositions of the present invention may be used as the adhesive component in pressure-sensitive tapes, films and foams. They adhere well to resin surfaces such as plasticized polyvinyl chloride, polyethylene terephthalate such as Mylar, cellulose acetate, nylon, polyethylene, polypropylene, paper, or silicone-coated paper as well as metal and painted surfaces. They are especially useful as the adhesive component of decorative vinyl sheets and decals, conferring excellent shrink resistance to vinyl film. Their excellent tack retention, creep resistance and resistance to plasticizer migration make them useful as adhesives for vinyl foam and tiles. Their outstanding tack, wetting and holding power may be used to advantage in transfer adhesive applications.

Articles of manufacture such as tapes, decals, decorative vinyl sheets and transfer films containing the pressure-sensitive resin composition of the present invention are prepared by coating the resin on the appropriate substrate by conventional coating methods. Such articles conventionally include a release paper for temporary protection of the adhesive film until the adhesive bond is made. The thickness of the adhesive film is generally in the range of 0.00051 to 0.0127 cm.

Application of the film to the substrate is conventionally carried out on roll coaters such as reverse roll and gravure roll coaters. The resin solution viscosity is adjusted to between 25 and 5,000 centipoises with higher viscosities within the range preferred for reverse roll coating and lower viscosities within the range preferred for gravure coating. The coatings are applied to the substrate moving through the rolls at a rate of between 5.1 cm/sec. and 508.0 cm/sec.

Example C.
This Example is set forth to compare the performance of a resin solution formulated with tetrabutyl titanate with a resin solution formulated with diisopropoxy titanium diacetylacetone in reverse roll application to a poly(vinyl chloride) substrate at a rate of 25.4 cm/sec.

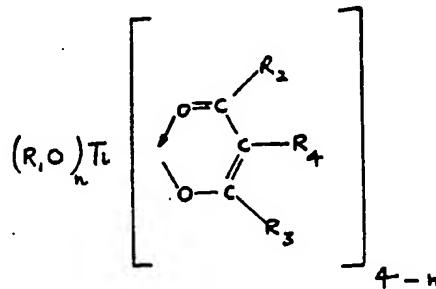
Polymer solutions made according to preparation Example 1 are diluted to 30 per cent solids and formulated with 0.5 parts tetrabutyl titanate or diisopropoxy titanium diacetylacetone per 100 parts of resin. The levels of titanate compound are selected to give the desired cohesive strength in the dried films. The TBT solution had a Stringiness Index of about 0.45 and gives poor coatings of rough

surface texture and uneven thickness. A large number of "strings" are observed between the application roll and the substrate during the coating operation. These coatings are judged unsuitable for commercial use. The TAA solution has a Stringiness Index of about 0.20 and gives smooth coatings of uniform thickness. These films are judged satisfactory for commercial use.

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WHAT WE CLAIM IS:—

1. An organic solvent solution comprising:
 - (i) a chelate ester having the formula



10 wherein n is 2 or 3, R₁ is a C₂ to C₁₀ alkyl, alkenyl, substituted alkyl or substituted alkenyl group, R₂ is a C₁ to C₆ alkyl, alkoxy, alkenyl or alkenoxy group, R₃ is a C₁ to C₆ alkyl or alkenyl group or a C₆ to C₁₀ aryl group and R₄ is hydrogen or a C₁ to C₆ alkyl or alkenyl group, and R₂ and R₃ may be combined as an ethylene or a trimethylene group; and

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15 (ii) an interpolymer comprising:

(A) between 0.5 and 20 weight per cent of at least one monomer containing a hydroxyl, carboxyl or enolizable keto group,

(B) at least one monomer which is an ester of acrylic acid or methacrylic acid containing from 6 to 20 carbon atoms, and optionally

20 (C) a monomer which is an α -olefin containing from 2 to 10 carbon atoms, a C₃ to C₁₀ vinyl alkanoate, an ethyl or methyl ester of acrylic or methacrylic acid, acrylonitrile, methacrylonitrile, styrene, or vinyl chloride, wherein the interpolymer has a weight average molecular weight in the range of 10,000 to 500,000 and a glass transition temperature in the

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25 range of -15 to -75°C.; wherein there are between 0.01 and 4 parts by weight of the chelate ester per 100 parts of interpolymer and wherein the stringiness index of the solution is less than 0.76 cm.

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30 2. A resin solution according to Claim 1 in which the chelate ester is the reaction product of a tetraalkyl or tetraalkenyl titanate wherein the alkyl or alkenyl group contains 2 to 10 carbon atoms, and an enolizable keto compound which is acetylacetone, benzoylacetone, 1,3-cyclopentandione, 1,3-cyclohexandione, or an alkyl acetoacetate or a C₁ to C₆ alkyl or alkenyl substituted derivative thereof, the mole ratio of tetraalkyl or tetraalkenyl titanate to enolizable keto compound being in the range of 1:1 to 1:2.

30

35 3. A resin solution according to Claim 2 in which the enolizable keto compound is acetylacetone.

35

40 4. A resin solution according to any of Claims 1 to 3 in which the interpolymer comprises a hydroxy monomer which is 2-hydroxyethyl acrylate or methacrylate, 2-hydroxypropyl acrylate or methacrylate, 3-hydroxypropyl acrylate or methacrylate, bis(2-hydroxyethyl) fumarate, or bis(2-hydroxyethyl) maleate.

40

45 5. A resin solution according to Claim 4 characterized wherein said interpolymer comprises 2-ethylhexyl acrylate and 2-hydroxyethyl acrylate.

45

6. A resin solution according to any of Claims 1 to 3 in which the interpolymer comprises a carboxy monomer which is acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, maleic acid, fumaric acid, citraconic acid, itaconic acid or an alkyl mono ester of maleic acid, fumaric acid, citraconic acid, or itaconic acid in which the alkyl group contains from 1 to 8 carbon atoms.

50 7. A resin solution according to any of Claims 1 to 3 in which the interpolymer comprises 2-ethylhexyl acrylate and acrylic acid, methacrylic acid, N,N-diacetonyl-acrylamide or N,N-diacetonylmethacrylamide.

50

8. A resin solution according to any of Claims 1 to 7 containing less than 3 weight per cent of water based on the total weight of the solvent. 5

9. A resin solution according to any of Claims 1 to 8 in which the solids content is from 10 to 60% by weight. 5

10. A resin solution according to Claim 1 in which the interpolymer is substantially as described in any one of Preparation Examples 1 to 11. 10

11. A resin solution according to Claim 1 substantially as described in the non-comparative portion of Example A. 10

12. A process for the production of film of pressure sensitive adhesive which comprises coating a substrate with a resin solution according to Claim 1, dispelling the solvent therefrom and curing the resulting film. 10

13. A process according to Claim 12 in which the substrate is a film of plasticized polyvinyl chloride, polyethylene terephthalate, cellulose acetate, nylon, polyethylene, polypropylene, paper or a silicone-coated paper. 15

14. A process according to either of Claims 12 and 13 in which the resin solution has the features of any one of Claims 2 to 11. 15

15. An article coated with a film of pressure-sensitive adhesive resin prepared by a process according to any of Claims 12 to 14. 15

16. A process for the production of an article according to Claim 15 substantially as described in Example B. 20

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